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**Japanese Patent Application JP 53 - 50088 A**

**A Method for the Manufacture of Spherical Activated Carbon**

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**For: Eastman Chemical Company**

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(54) Title of the Invention: **A Method for the Manufacture of Spherical Activated Carbon**

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**SPECIFICATION****1. Title of the Invention**

A Method for the Manufacture of Spherical Activated Carbon

**2. Claims**

(1) A method for the manufacture of spherical activated carbon, characterized in that a porous spherical organic polymer compound is rendered infusible and calcined, and the porous carbon that is obtained is activated, or said polymer compound is rendered infusible and is activated while being carbonized.

(2) A method as described in Claim 1, in which the porous spherical organic polymer compound is manufactured by means of a method in which a mixture of at least one unsaturated monomer and a monomer that contains several ethylenic unsaturated groups in an unconjugated relationship is subjected to suspension polymerization in an aqueous medium in the presence of a liquid precipitant that acts as a solvent for the mixture, is essentially insoluble in water, and does not cause swelling of the copolymer obtained by copolymerization.

(3) A method as described in Claim 3, in which the monomer that contains several ethylenic unsaturated groups in an unconjugated relationship is divinyl benzene and in which the monoethylenic unsaturated monomer is selected from styrene and acrylonitrile.

(4) A method as described in Claim 1, in which the infusibilizing treatment agent is sulfuric acid or anhydrous sulfuric acid.

(5) A method as described in Claim 1, in which the activated carbon has a pore diameter of 50 to 10,000 Å and a pore volumetric capacity of 0.3 cc/g or greater.

### **3. Detailed Description of the Invention**

The present invention relates to a novel method for the manufacture of spherical activated carbon.

The conventional method for making spherical carbon is one in which powdered carbon is mixed with a binder and is molded into a spherical shape. However, this method is disadvantageous in that the powder is difficult to handle during molding and that the spheres have an irregular morphology; i.e., it is difficult to obtain a perfectly spherical shape. There are further drawbacks in that it is extremely difficult to obtain fine spherical carbon with particle diameters of from several tens of microns to 1 mm, that the surface strength of the material as spherical carbon is low and that it tends to become finely powdered. Consequently, there is a desire for a variety of reasons to manufacture good-quality spherical carbon with good efficiency, something that cannot be achieved by conventional means.

Further, as a result of the rapidly advancing environmental pollution in recent years, it has been recognized that the use of activated carbon is extremely effective for the purposes of various treatments of industrial wastewater, purification of drinking water and desulfurization of flue gas, and there is a strong desire for technologies that would make it possible to achieve stable and satisfactory manufacture of activated carbon in large volume at low cost. However, in conventional methods for the manufacture of activated carbon, the principal raw materials are woody materials such as wood scraps and coconut husks, so that limitations of resources cannot be avoided. Most recently, manufacture of activated carbon using coal has been attempted. However, in this case as well, the raw materials are natural substances and there are great differences in their properties depending on their region of production, for which reason there is a major problem in the assurance of homogeneous, stable raw materials. Consequently, the development of new raw materials for the stable and satisfactory manufacture of activated carbon in large volumes at low cost is the first major problem in the manufacture of activated carbon at present.

The second problem is the problem of activated carbon use. Molded activated carbon is ordinarily used by passing a gas or liquid through the activated carbon layer to bring the two into contact with each other. Consequently, ease of operation, stable passage of gases and liquids, and other operating aspects must be assured. The shape and strength of the activated carbon, and, in particular, the scale of production are major factors for this purpose. In terms of shape, spherical activated carbon is better than activated carbon of irregular shapes such as cylindrical activated carbon. This is because uniform contact is possible and there is little resistance to the passage of air and fluids. Fine fragments and fine powders are less likely to be produced during service than with other shapes. Consequently, various spheroidizing methods have been proposed. There is also a method in which, when powdered carbon materials that have been prepared in advance are mixed with binders, a spherical shape is made by such means as tumbling granulation, and the binder is then carbonized, after which the carbon is reactivated to make spherical activated carbon. In this method as well, production of fine powder cannot be avoided and there are many impediments such as scattering of fine particles during handling of the activated carbon, an increase of flow resistance due to the fine particles during passage of gas and fluids, and admixture of the fine powder into the gas or liquid after the activated carbon treatment.

The third problem is that adsorption capacity decreases in comparison with fine powdered activated carbon when the material is made into spherical carbon. Thus, there is a desire for the development of a method for manufacturing activated carbon of better adsorptive capacity.

The inventors first discovered a method for the manufacture of stable porous carbon (Japanese Patent Application 50-107762 [1975] and Japanese Patent Application 50-107763 [1975]).

When this porous spherical carbon is subjected to activation treatment by standard methods, a stable, fine powder is not produced. Moreover, because of the presence of pores through which solution can slowly penetrate, a discovery was made that it was possible to manufacture activated carbon whose adsorption capacity would be better than that of the spherical activated carbon existing at that time.

This invention is based on these findings and is a result of the discovery that spherical activated carbon of superior adsorption capacity can be manufactured by infusibilizing, calcining and activating porous organic polymer compounds.

The porous spherical carbon in this invention is a substance in which pores whose pore range from 10, to 50,000 Å are contained in an amount of 0.1 cc/g or greater.

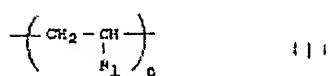
The amount of pores with pore diameters of 50, to 10,000 Å is preferably 0.3 cc/g or greater. When the pore diameter is less than this, penetration of solution to the interior is insufficient and adsorption capacity is decreased. When the pore diameter is greater than this, strength is decreased. Adsorption capacity is also decreased when the quantity of pores is less than that indicated above.

The first method for manufacturing porous spherical organic polymers is one in which a polymer serves as a starting material. Means for creating porosity include (1) foaming methods in which a foaming agent that is decomposed by heating and that produces a gas is introduced into the polymer and molding is performed, after which the foaming agent is decomposed by heating and a gas is produced, (2) elution methods as represented by a method in which a water-insoluble organic polymer and a water-soluble polymer are mixed, after which the mixture is molded, the molded product is immersed in water and a water-soluble polymer is extracted and (3) sol-gel transfer methods in which a solution of the polymer is brought into contact with a solution that is miscible with the solvent but cannot dissolve the polymer. Means for making this

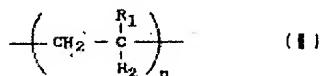
solution into a sphere include (1) methods of drying in water in which the polymer is dissolved in a low-boiling solvent, this solution is suspended in water and the solvent is removed at a temperature between the boiling point of the solvent and the boiling point of water, (2) an orifice method in which a polymer solution is spheroidized using an orifice and is added in drops to a nonsolvent and (3) a melting-dispersion-cooling method in which spheres are made by adding a fine powder of polymer to a dispersing medium, raising the temperature to near the softening point of the polymer and stirring, with the polymer then being gradually cooled.

A porous carbon precursor can be obtained by combining a method for creating porosity with a method for making spheres. As an example, there is a method in which a spherical porous body can be obtained by a process in which the polymer and a foaming agent are dissolved in chloroform and suspended in water, after which the chloroform is removed by drying in solution and the spheres that are obtained are foamed at a high temperature, or a method in which a water-insoluble polymer is dissolved in a solvent that is miscible with water, such as formamide or dimethyl sulfoxide, and the product is added in drops to water by the orifice technique, whereupon a sol-gel transfer occurs in the water and a spherical porous body is obtained. There is also a method in which a water-insoluble polymer and water-soluble polymer are blended, the blend is made into a fine powder, the powder is then spheroidized by causing the material to undergo melting, dispersing and cooling in silicone oil, and the water-soluble polymer in the water is removed.

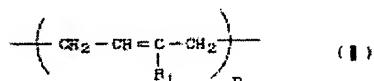
The polymers that can be used include, for example, polymers that are obtained from monomers having vinyl groups comprised; namely, polymer comprised of alkyl vinyl compounds, such as polyethylene and polypropylene; polymers comprised of aryl vinyl compounds, such as polystyrene and polyvinyl naphthalene; polymers comprised of vinyl ethers, such as polyethyl vinyl ether and polyisobutyl vinyl ether; polymers comprised of vinyl halide compounds, such as such as polyvinyl chloride; polymers comprised of vinyl ester compounds, such as polyvinyl acetate; polymers comprised of alkyl vinyl esters, such as polymethyl acrylate; and polymers comprised of vinyl nitriles such as polyacrylonitrile, which polymers are represented by the general formula



[wherein, R<sub>1</sub> is hydrogen, a hydrocarbon group, a substituted hydrocarbon group, a hydrocarbonoxy group, a substituted hydrocarbonoxy group, a halogen, a cyano group, an hydroxyl group, -OCOR<sub>2</sub> or -COOR<sub>2</sub> (R<sub>2</sub><sup>1</sup> being hydrogen, a hydrocarbon group or a substituted hydrocarbon group) and n is an integer that represents the degree of polymerization]; polymers obtained from monomers having vinylidene groups; namely, polymers comprised of alkyl or aryl vinylidene compounds, such as polyisobutylene and  $\alpha$ -methylstyrene; polymers comprised of vinylidene halide compounds, such as polyvinylidene chloride; polymers comprised of  $\alpha$ -alkyl acrylic acid esters, such as polymethyl methacrylate and polyethyl methacrylate; and polymers comprised of cyanovinylidene, such as polycyanovinylidene, which polymers are represented by the general formula



[wherein, R<sub>1</sub> and R<sub>2</sub> are hydrocarbon groups, substituted hydrocarbon groups, hydrocarbonoxy groups, substituted hydrocarbonoxy groups, halogens, cyano groups, -OCOR<sub>3</sub> or -COOR<sub>3</sub> (R<sub>3</sub> being hydrogen, a hydrocarbon group or a substituted hydrocarbon group) and n is an integer that represents the degree of polymerization]; polymers comprised of monomers having conjugated double bonds, such as polybutadiene, polyisoprene and polychloroprene (neoprene), which polymers are represented by the general formula



[wherein, R<sub>1</sub> is hydrogen, a hydrocarbon group, a substituted hydrocarbon group, a hydrocarbonoxy group, a substituted hydrocarbonoxy group, a halogen, a cyano group, -OCOR<sub>1</sub> or -COOR<sub>1</sub> (R<sub>1</sub> being hydrogen, a hydrocarbon group or a substituted hydrocarbon group) and n is an integer that represents the degree of polymerization]; copolymers comprised of the monomers of polymers represented by general formula (I) or general formula (II), such as ethylene-propylene copolymers, ethylene-propylene-dichloropentadiene ternary copolymers, ethylene-propylene-ethylidene norbornene ternary copolymers, styrene-acrylonitrile copolymers,

<sup>1</sup> Translator's note: There is no "R<sub>2</sub>" in the formula.

styrene-acrylonitrile-butadiene ternary copolymers, ethylene-vinyl acetate copolymers, styrene-butadiene copolymers (including SBR and impact-resistant polystyrene), butadiene-acrylonitrile copolymers, ethylene-isobutylene-butadiene ternary copolymers, ethylene terephthalate- $\beta$ -chloroethyl vinyl ether copolymers, butyl acrylate-acrylonitrile copolymers, ethylene trifluoride-vinylidene fluoride copolymers, vinylidene fluoride-hexafluoropropylene copolymers, vinyl chloride-ethylene copolymers, vinyl chloride-propylene copolymers, normal butadiene-isobutene copolymers, isobutylene-isoprene copolymers, acrylonitrile-methyl acrylate copolymers, acrylonitrile-vinyl acetate copolymers, acrylonitrile-methyl methacrylate copolymers, acrylonitrile-acrylic acid copolymers, acrylonitrile-methacrylic acid copolymers, acrylonitrile-vinyl chloride copolymers, acrylonitrile-vinylidene chloride copolymers and vinyl chloride-vinylidene chloride copolymers or graft copolymers thereof; polyesters such as polyethylene terephthalate, polyethylene isophthalate, polyethylene fumarate, polypropylene maleate and poly p-phenylene oxybenzoate; polyamides such as polycaproamide (nylon 6) and polyhexamethylene dipolyamide (nylon 66); polyalkylene ethers and poly-substituted alkylene ethers such as polyoxymethylene, polyethylene oxide and polybis(chloromethyl)oxyethane; polyphenylene oxides such as poly-2,6-dimethyl-1,4-phenylene oxide and poly-2,6-diphenyl-1,4-phenylene oxide; and polymers in which bisphenol A is the monomer, such as bisphenol A-epichlorohydrin polymers, bisphenol A-phosgene polymers and bisphenol A-4,4'-diphenylsulfone polymers, as well as polyphenylene, polyxylylene, polybenzimidazole, polybenzimidazoimide, polyimidazopyrrolone, polypyromellitimide, polybenzothiazole, polythiazole, polyquinazolone, polyquinoxaline, polybenzoxazole and polyoxadiazole. In addition, pitches obtained by petroleum refining and dry distillation of coal can also be used.

These polymers can be used individually or two or more of them can be used at the same time. In addition, these polymers can be used mixed with other suitable organic substances in any desired composition.

Of these, polymers or copolymers in which the principal component is one or more of styrene, divinyl benzene, acrylonitrile and 2,6-dimethyl-1,4-phenylene oxide are desirable.

The second method of making porous, spherical organic polymers is one in which a monomer is used as a starting material and in which the spherical shape is made using suspension polymerization technology. Methods for obtaining porous bodies include (1) a method in which a monomer and a substance that is soluble in a nonsolvent of the monomer's

polymer are placed together and suspension polymerization is performed, with the other substances that are present being removed during polymerization, and (2) a method in which suspension polymerization is performed in the presence of a solvent (precipitant) that is soluble in the monomer but does not cause the polymer to swell. Method (2) is described in the specification of Japanese Patent Application 50-107763 [1975].

The monomers that can be used in this case are divinyl benzene, divinyl pyridine, divinyl toluene, divinyl naphthalene, diallyl phthalate, ethylene glycol diacrylate, ethylene glycol dimethacrylate, divinyl xylene, divinyl ethyl benzene, divinyl sulfone, glycol, glycerol, pentaerythritol, monothio or dithio derivatives of glycol, polyvinyl or polyallyl ethers of resorcin, divinyl ketone, divinyl sulfide, allyl acrylate, diallyl maleate, diallyl fumarate, diallyl succinate, diallyl carbonate, diallyl malonate, diallyl oxalate, diallyl adipate, diallyl sebacate, divinyl sebacate, diallyl tartrate, diallyl silicate, triallyl tri-1-naphthyl methylcarbamate, triallyl aconitate, triallyl citrate, triallyl phosphate, N,N'-methylene diacrylamide, N,N'-methylene dimethacrylamide, N,N'-ethylene diacrylamide, 1,2-di( $\alpha$ -methyl methylene sulfonamido)-ethylene, trivinyl benzene, trivinyl naphthalene and polyvinyl anthracene.

Monoethylene unsaturated monomers include methyl acrylate, ethyl acrylate, propyl acrylate, isopropyl acrylate, butyl acrylate, tert-butyl acrylate, ethylhexyl acrylate, cyclohexyl acrylate, isobornyl acrylate, benzyl acrylate, phenyl acrylate, alkyl phenyl acrylate, ethoxymethyl acrylate, ethoxyethyl acrylate, ethoxypropyl acrylate, propoxymethyl acrylate, propoxyethyl acrylate, propoxypropyl acrylate, ethoxyphenyl acrylate, ethoxybenzyl acrylate, ethoxycyclohexyl acrylate, corresponding esters of methacrylic acid, styrene, vinyl toluene, vinyl naphthalene, acrylonitrile and similar unsaturated monomers.

It is also possible to use monovinylidene compounds having nitrogen heterocyclic ring compounds, such as vinyl pyridine, 2-methyl-5-vinyl pyridine, 2-ethyl-5-vinyl pyridine, 3-methyl-5-vinyl pyridine, 2,3-dimethyl-5-vinyl pyridine, 2-methyl-3-ethyl-5-vinyl pyridine, 2-methyl-5-vinyl quinoline, 4-methyl-4-vinyl quinoline, 1-methyl or 3-methyl-5-vinyl isoquinoline and vinyl pyrrolidone. It is further possible to use mixtures of the aforementioned monomers with monovinylene compounds, such as dialkyl maleates, dialkyl fumarates, dialkyl crotonates, dialkyl itaconates and dialkyl gluconates.

Method (2) is a method that is suited to the objectives of this invention. A specific example of this method is one in which a mixture of styrene, acrylonitrile or another

monoethylenic unsaturated monomer with divinyl benzene, trivinyl benzene or another ethylenic unsaturated monomer that has several ethylenic unsaturated groups in an unconjugated relationship is subjected to suspension copolymerization in an aqueous medium in the presence of n-butanol, heptane or another precipitant that acts as a solvent for the mixture, is essentially a water-insoluble liquid and does not cause swelling in the copolymer obtained by copolymerization.

The porous spherical organic polymer that has been obtained by this method is subjected to an infusibilizing treatment by such methods as sulfonation and nitration, and porous spherical carbon is obtained by calcination at a temperature of 500°C, and, preferably 800°C to 3000°C.

The porous spherical carbon that has been obtained in this way can be converted to activated carbon by a known method, for example, by activation at a temperature of 800 to 1200°C in accordance with the water vapor method.

The material obtained by subjecting the porous spherical organic polymer compound to an infusibilizing treatment is gradually carbonized by heating the system in a water vapor atmosphere. The temperature increase is stopped when the temperature reaches 800 to 1200°C, and activation can be performed while this temperature is maintained and carbonization is being performed.

The spherical, porous carbon that has been obtained in this way is superior to fine powdered activated carbon in adsorption capacity in solutions, is perfectly spherical, has high strength and does not generate fine powder.

The activated carbon that is obtained in this invention as described above exhibits little power forming properties, is of high strength and is superior as a water treatment agent, catalyst or catalyst carrier.

### **Working Example 1**

5.0 g of polyvinyl alcohol, 6.7 g of carboxymethyl cellulose and 56 g of NaCl were dissolved in 1.5 liters of distilled water, a mixture of 200 g of styrene, 145.5 g of divinyl benzene (55% of the commercial product) and 1.5 g of benzoyl peroxide was added and the materials were reacted for 6 hours at 85°C under stirring. The bulk density of the copolymer that was obtained was 0.39. The copolymer thus obtained (40 g) was subjected to a sulfonation reaction for 6 hours at 110°C in 500 g of 15% fuming sulfuric acid. Next, calcination was performed in

$N_2$  at a temperature elevation rate of 300°C/hour up to 1000°C. The bulk density was 0.55. The average pore diameter was 200 Å, and the material contained fine pores of 50 Å or greater in an amount of 0.6 g/cc.

The porous spherical carbon was activated for 2 hours at 800°C in a water vapor atmosphere. Spherical activated carbon with a surface area of 1100  $m^2/g$  was obtained.

Fig. 1 shows the methylene blue adsorption curves of commercial spherical carbon and commercial powdered activated carbon by comparison to that of the spherical activated carbon in question.

As should be evident from the results, the spherical activated carbon obtained in this invention is superior in adsorption capacity to powdered activated carbon.

#### 4. Brief Description of the Drawings

Fig. 1 shows the methylene blue adsorption curves of activated carbon based on this invention and of commercial activated carbon pertaining to a comparison example.

1 shows the product of this invention, 2 shows commercial powdered activated carbon and 3 shows commercial granular activated carbon.

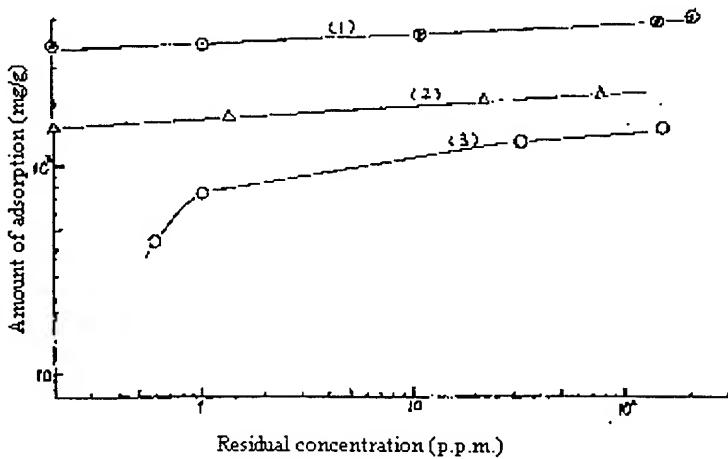


Fig. 1

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(全 6 頁)

⑯球状活性炭の製造法

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⑯出 願 昭51(1976)10月19日  
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明細書

1. 発明の名称

球状活性炭の製造法

2. 特許請求の範囲

(1) 多孔質球状有機高分子化合物を不融化し、焼成して得られる多孔質炭素を賦活するかあるいは該高分子化合物を不融化し、炭化しながら賦活することを特徴とする球状活性炭の製造法。

(2) 多孔質球状有機高分子化合物が、非共役関係にある複数個のエチレン系不饱和基を含有する单量体と少くとも1種のモノエチレン系不饱和单量体との混合物を、この混合物の溶剤として作用する実質的に水不溶性の液体であってかつ共重合して得られた共重合体を膨潤させない沈殿剤の存在下で、水性媒体中で懸濁共重合させる方法によって製造されたものである特許請求の範囲第1項記載の方法。

(3) 非共役関係にある複数個のエチレン系不饱和基を含有する单量体がジビニルベンゼンで

あり、かつモノエチレン系不饱和单量体がステレンおよびアクリロニトリルから選ばれたものである特許請求の範囲第3項記載の方法。

(4) 不融化処理剤が硫酸または無水硫酸である特許請求の範囲第1項記載の方法。

(5) 活性炭が孔径50~10,000Åおよび孔の容積量0.3cc/g以上を有する特許請求の範囲第1項記載の方法。

3. 発明の詳細な説明

本発明は球状活性炭の新規製造法に関する。球状炭素を作る方法としては、従来粉状炭を粘結剤と混合し、球状に成形するという方法が用いられているが、成形時粉体を取扱うことによる作業性の低下、球の形態の不整、即ち真球状のものが得難い欠点がある。又直径1mm以下数十μに至る細かい球状炭を得る事は極めて困難であり、球状炭としても表面強度が低く微粉化し易い欠点を示す。従って従来得られなかつた良質の球状炭を効率良く製造する事が各方面より要望せられていた。

又、近年環境汚染が急速に進行した結果、各種産業排水の処理、飲料水の浄化、排煙脱硫のために活性炭を用いることは極めて効果的である事が認識され低成本で大量、安定且つ良好な活性炭を製造する技術が強く望まれている。しかし従来活性炭の製造は木屑、ヤシ殻等の木質系のものが主原料であり資源的な限界が避けられない。又最近石炭を原料として活性炭の製造が試みられているが、この場合も原料は天然物であり、产地により、その特性は大幅に変化するため、均質安定な原料確保に大きな問題がある。従って低成本で大量安定に良好な活性炭を製造するための新しい原料を開発することが、現在活性炭製造上の第一の大きな問題である。

第二の課題は活性炭使用上の問題である。成形活性炭は通常活性炭層に気体又は液体を通過させる事により両者を接触させて用いられる。従って良好な作業性、安定な通気、通液等の操作性が確保されねばならないが、その為には活

性炭の形状、強度特に微粉の生成度合等が大きな因子となる。形状に関しては円筒状活性炭等の不整形活性炭に比較して、球形活性炭が最も好ましいとされている。何故ならば均一な接触が可能であるとともに通気、通液抵抗が少ないからである。又他の形状に比し作用中に細かい破片や、微粉が生成しにくいことである。従って各種の球形成形法が提案せられている。しかし、何れも予め調整された粉末炭素材料を粘結剤と混合し、転動造粒等の手段により球形とし、次いで粘結剤を炭化後賦活して、球形活性炭とする方法である。この方法においても微粉の生成は避けられず、活性炭取扱い時の微粉の飛散、通気、通液時の微粉による流れ抵抗の上昇、活性炭処理後の気体液体中への微粉の混入等の多くの支障を生ずる。

第三の課題として球状炭にすると微粉末の活性炭に比し吸着能の低下がみられ、吸着能のすぐれた球状活性炭の製造法の開発が望まれている。

本発明者らは先に強固な多孔質炭素の製造法を見いだした(特願昭50-107742、特願昭50-107743)。

この多孔質球状炭素を通常の方法で活性化処理を行うと、強固で微粉末の発生がなく、しかも溶液が浸透してゆくことができる孔が存在するため、これ迄の球状活性炭よりもすぐれた吸着能を有する活性炭を製造し得ることを見いだした。

本発明はかかる知見を基にして、多孔質有機高分子化合物を不融化焼成し賦活することにより吸着能のすぐれた球状活性炭を製造できることを見出したものである。

本発明において多孔質球状炭素とは孔径10~50,000Åの細孔を0.1cc/g以上有するものである。

望ましくは50Å~10,000Åの細孔を0.3cc/g以上有するものである。孔径がこれ以下であると溶液の内部の浸透が不十分であり吸着能が低下する。これ以上になると強度的に弱く

なる。又細孔量がこれ以下であっても吸着能が低下する。

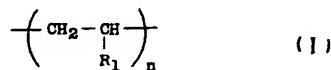
多孔質球状有機高分子を製造する方法としては、第一の方法として高分子から出発する方法がある。多孔性にする手段としては(1)高分子中に加熱により分解して気体を発生する発泡剤を混入し成形後加熱により発泡剤を分解させ気体を発生させる発泡法、(2)非水溶性有機高分子と水溶性高分子を混合した後成形し成形物を水中に浸漬し水溶性高分子を抽出させる方法に代表される溶出法、(3)高分子の溶液を溶剤と混じり合い高分子の非溶剤である液と接触させるソルゲル転移法がある。この溶液を球状化を行う手段としては(1)高分子を水より沸点の低い溶剤にとかしこの溶液を水中に懸濁し、水の沸点以下、溶剤の沸点以上の温度で溶剤を除去する水中乾燥法、(2)高分子の溶液をオリフィスを用いて球状化し非溶媒中に落下させるオリフィス法、(3)分散媒中に高分子の微粉を加え高分子の軟化点付近昇温し攪拌を行うことによって球状化

し徐々に冷却する融解分散冷却法等がある。

この多孔性にする方法と球状化の方法を結びつけることによって多孔性炭素前駆体を得ることができる。例を示すと高分子と発泡剤をクロロホルムに溶かし水中に懸濁した後液中乾燥でクロロホルムを除去し得られた球状体をさらに高温で発泡せしめる方法、非水溶性高分子をホルムアミド、ジメチルスルホキシドの極な水と混じり合う溶媒に溶かしオリフィス法によって水中に滴下すると、水中においてソルーベル転移がおこり球状多孔体を得ることができる。非水溶性高分子と水溶性高分子をブレンド後酸化しシリコーン油の中で融解分散冷却法によって球状化した後、水中で水溶性高分子を除去する方法などである。

ここで用いられる高分子としては、例えはポリエチレン、ポリプロピレンなどのアルキルビニル化合物からの重合体、ポリスチレン、ポリビニルナフタレンなどのアリールビニル化合物からの重合体、ポリエチルビニルエーテル、ボ

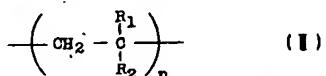
リソブチルビニルエーテルなどのビニルエーテルからの重合体、ポリ塩化ビニルなどのハロゲン化ビニル化合物からの重合体、ポリ酢酸ビニルなどのビニルエステル化合物からの重合体、ポリメチルアクリレートなどのアクリル酸エステル類からの重合体、ポリアクリロニトリルなどのビニルニトリルからの重合体など、ビニル基を有する単量体から得られる重合体で一般式



(ただし、 $\text{R}_1$ は水素、炭化水素基、置換炭化水素基、ハイドロカルボノキシ基、置換ハイドロカルボノキシ基、ハロゲン、シアノ基、水酸基、 $-\text{OCOR}_2$ 、 $-\text{COOR}_2$  ( $\text{R}_2$ は水素、炭化水素基、置換炭化水素基)、 $n$ は重合度を表わす整数である。)

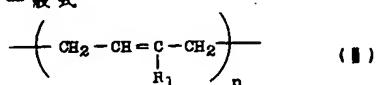
で表わされる重合体、またポリソブチレン、ポリエーメチルスチレンなどのようなアルキルまたはアリールビニリデン化合物からの重合体、ポリ塩化ビニリデンなどのハロゲン化ビニリデ

ン化合物からの重合体、ポリメチルメタクリレート、ポリエチルメタクリレートなどの $\alpha$ -アーチカルキルアクリル酸エステルからの重合体、ポリシアノビニリデンなどのシアノビニリデンからの重合体などビニリデン基を有する単量体から得られる重合体で、一般式



(ただし、 $\text{R}_1$ 、 $\text{R}_2$ は炭化水素基、置換炭化水素基、ハイドロカルボノキシ基、置換ハイドロカルボノキシ基、ハロゲン、シアノ基、 $-\text{OCOR}_3$ 、 $-\text{COOR}_3$  ( $\text{R}_3$ は水素、炭化水素基、置換炭化水素基)、 $n$ は重合度を表わす整数である。)

で表わされる重合体、またポリブタジエン、ポリソブレン、ポリクロロブレン(ネオブレン)などの共役二重結合を有する単量体からの重合体で、一般式



(ただし、 $\text{R}_1$ は水素、炭化水素基、置換炭化水素基、ハロゲン、シアノ基、 $-\text{OCOR}_1$ 、 $-\text{COOR}_1$  ( $\text{R}_1$ は水素、炭化水素基、置換炭化水素基)、 $n$ は重合度を表わす整数である。)

で表わされる重合体、またエチレン-プロピレン共重合体、エチレン-プロピレン-ジシクロベントジエン三元共重合体、エチレン-プロピレン-エチリデンノルボルネン三元共重合体、ステレン-アクリロニトリル共重合体、ステレン-アクリロニトリル-ブタジエン三元共重合体、エチレン-酢酸ビニル共重合体、ステレン-ブタジエン共重合体(SBR、耐衝撃性ポリスチレンを含む)、ブタジエン-アクリロニトリル共重合体、エチレン-イソブチレン-ブタジエン三元共重合体、エチルアクリレート- $\beta$ -クロルエチルビニルエーテル共重合体、ブチルアクリレート-アクリロニトリル共重合体、三フッ化エチレン-二フッ化ビニリデン共重合体、二フッ化ビニリデン-ヘキサフルオロブロピレン共重合体、塩化ビニル-エチレン共重合体、塩

化ビニルーブロビレン共重合体、ノルマルブテン-1-イソブテン共重合体、イソブチレン-1-イソブレン共重合体、アクリロニトリル-アクリル酸メチル共重合体、アクリロニトリル-酢酸ビニル共重合体、アクリロニトリル-メタクリル酸メチル共重合体、アクリロニトリル-アクリル酸共重合体、アクリロニトリル-メタアクリル酸共重合体、アクリロニトリル-塩化ビニル共重合体、アクリロニトリル-塩化ビニリデン共重合体、塩化ビニル-塩化ビニリデン共重合体など一般式(I)または(II)または(III)で示される重合体の単量体からの共重合体、もしくはこれらのグラフト共重合体、ポリエチレンテレフタレート、ポリエチレンイソフタレート、ポリエチレンマレート、ポリブロビレンマレート、ポリバラエチレンオキシベンゾエートなどのポリエステル、ポリカブロアミド(ナイロン-6)、ポリヘキサメチレンジポリアミド(ナイロン-6,6)などのポリアミド、ポリオキシメチレン、ポリエチレンオキシド、ポリビスクロルメチル

オキシエタンなどのポリアルキレンエーテル、ポリ置換アルキレンエーテル、ポリ-2,6-ジメチル-1,4-フェニレンオキシド、ポリ-2,6-ジフェニル-1,4-フェニレンオキシドなどのポリフェニレンオキシド、ビスフェノールA-エビクロルヒドリン重合体、ビスフェノールA-ホスゲン重合体、ビスフェノールA-4,4'-ジフェニルスルホン重合体などビスフェノールAを一単量体とする重合体、その他ポリフェニレン、ポリキシリレン、ポリベンツイミダゾール、ポリベンツイミダゾイミド、ポリイミダゾビロロン、ポリビロメリットイミド、ポリベンツチアゾール、ポリチアゾール、ポリキナゾロン、ポリキノキサリン、ポリベンツオキサゾール、ポリオキサジアゾールなどの重合体があげられる。また石油精製、石炭乾留などによって得られるビッテを使用することもできる。

これら重合体は単独または二種以上を同時に用いることができる。またこれら重合体と他の

適当な有機物を任意の組成で混合して用いることも可能である。

これらの中でもステレン、ジビニルベンゼン、アクリロニトリル、2,6-ジメチル-1,4-フェニレンオキシドのうちの一又は二以上を主成分とする重合体あるいは共重合体が好ましい。

多孔質球状有機高分子をつくる第二の方法としては単量体から出発するものであって懸濁重合技術を用いて球状化をはがるものである。多孔体を得る方法としては(I)単量体とその重合体の非溶剤に可溶な物とを共存せしめて懸濁重合を行い、重合時共存物を除去する方法、(II)単量体に可溶であり、その重合体を膨潤せしめない溶剤(沈没剤)の存在下で懸濁重合を行う方法などである。(II)の方法は特願昭50-107763号明細書に記載されている。

ここで用いられる単量体としては、ジビニルベンゼン、ジビニルビリジン、ジビニルトルエン、ジビニルナフタレン、フタル酸ジアリル、

ジアクリル酸エチレングリコール、ジメタクリル酸エチレングリコール、ジビニルキシレン、ジビニルエチルベンゼン、ジビニルスルホン、グリコール、グリセリン、ベンタエリスリトール、グリコールのモノチオ或はジチオ誘導体、及びレゾルシン等のポリビニル或はポリアリルエーテル、ジビニルケトン、硫化ジビニル、アクリル酸アリル、マレイン酸ジアリル、フマル酸ジアリル、コハク酸ジアリル、炭酸ジアリル、マロン酸ジアリル、シウ酸ジアリル、アビシン酸ジアリル、セバシン酸ジアリル、セバシン酸ジビニル、酒石酸ジアリル、ケイ酸ジアリル、トリカルバリル酸トリアリル、アコニット酸トリアリル、クエン酸トリアリル、リン酸トリアリル、N,N'-メチレンジメタクリルアミド、N,N'-エチレンジアクリルアミド、N,N'-メチルメチレンスルホンアミド)エチレン、トリビニルベンゼン、トリビニルナフタレン及びポリビニルアンスラセンなどがあげられる。

モノエチレン不飽和単量体としては、アクリル酸メチル、アクリル酸エチル、アクリル酸ブロビル、アクリル酸イソプロビル、アクリル酸ブチル、アクリル酸第3級ブチル、アクリル酸エチルヘキシル、アクリル酸シクロヘキシル、アクリル酸イソボルニル、アクリル酸ベンジル、アクリル酸フェニル、アクリル酸アルキルフェニル、アクリル酸エトキシメチル、アクリル酸エトキシエチル、アクリル酸エトキシプロビル、アクリル酸プロポキシメチル、アクリル酸プロポキシエチル、アクリル酸プロポキシプロビル、アクリル酸エトキシフェニル、アクリル酸エトキシベンジル、アクリル酸エトキシシクロヘキシル、及びメタクリル酸の上記対応するエステル、ステレン、ビニルトルエン、ビニルナフタリン、アクリロニトリル及び同様不飽和単量体である。

また、ビニルビリジン、2-メチル-5-ビニルビリジン、2-エチル-5-ビニルビリジン、3-メチル-5-ビニルビリジン、2,3-

ジメチル-5-ビニルビリジン、及び2-メチル-3-エチル-5-ビニルビリジン、2-メチル-5-ビニルキノリン、4-メチル-4-ビニルキノリン、ノーメチル或は3-メチル-5-ビニルイソキノリン及びビニルビロリドンの如き蜜素複素環式化合物を有するモノビニリデン化合物も用いられる。また、上記単量体と、マレイン酸ジアルキル、スマル酸ジアルキル、クロトン酸ジアルキル、イタコン酸ジアルキル及びグルタコン酸ジアルキルの如きモノビニレン化合物との混合物も使用できる。

本発明の目的で適当であるのは(2)の方法である。該方法による具体例としては、ステレン、アクリロニトリルの様なモノエチレン系不飽和単量体とジビニルベンゼン、トリビニルベンゼンの様な非共役関係にある複数個のエチレン系不飽和基を含有するエチレン系不飽和単量体の混合物を正一ブタノール、ヘプタンの様な混合物の浴媒として作用し実質的に水不溶性の液体であってかつ共重合して得られた共重合体を膨

潤させない沈殿剤の存在下で水性媒体中で懸濁共重合する方法である。

この様な方法で得られた多孔質球状有機高分子をスルホン化、ニトロ化などの様な方法で不融化解処理し、500°C好ましくは800°C以上3000°C以下の温度まで焼成することによって多孔質球状炭素が得られる。

かくして得られた多孔質球状炭素は公知方法、例えば水蒸気法により800~1200°Cの温度で賦活することにより活性化炭素を得ることができる。

また多孔質球状有機高分子化合物を不融化解処理したものを水蒸気雰囲気中で昇温処理することにより次第に炭化させ800~1200°Cに達した時に昇温を停止し、この温度に維持して炭化させながら賦活を行うこともできる。

かくして得られた球状多孔質炭素は特に溶液中の吸着能において微粉状活性炭よりもすぐれ真球状であって強固で微粉末の発生をおこさない。

上記の如く本発明で得られた活性炭は粉化性が少なく強度が大であり、水処理剤、触媒、触媒担体としてすぐれたものである。

#### 実施例1

ポリビニルアルコール5.0g、カルボキシメチルセルローズ4.7g、NaCl 5.6gを蒸留水1.5Lに溶解しステレン200g、ジビニルベンゼン(市販品55%)145.5g、過酸化ベンゾイル1.5gを混合したものを加え、攪拌下85°C6時間反応せしめた。得られた共重合体の嵩比重は0.39であった。かくして得られた共重合体40gを15%発煙硫酸500gの中で110°C6時間スルホン化反応を行いH<sub>2</sub>SO<sub>4</sub>洗滌後水洗し乾燥を行った。ついでH<sub>2</sub>中300°C/hrの昇温速度で1000°C迄焼成した。嵩比重0.55であった。平均孔径200Åで50Å以上の細孔を0.6g/100g含んでいる。

この多孔質球状炭素を水蒸気雰囲気中800°Cで2時間賦活を行った。表面積1100m<sup>2</sup>/g

の球状活性炭が得られた。

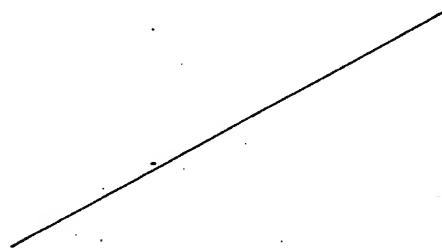
この球状活性炭及び比較として市販球状活性炭及び市販粉末活性炭のメチレンブルーの吸着曲線を第1図に示す。

これより明らかなる様に本発明において得られた球状活性炭は吸着能において粉末活性炭よりもすぐれている。

#### 4. 図面の簡単な説明

第1図は本発明による活性炭および比較試料である市販の活性炭のメチレンブルー吸着曲線を示す。

1は本発明品、2は市販粉末活性炭、3は市販粒状活性炭を示す。



第1図

